

TITLE: HINDERED DIFFUSION OF ASPHALTENES
AT EVALUATED TEMPERATURE AND PRESSURE

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ABSTRACT

Our overall project objective is to obtain fundamental information on the diffusion of coal and petroleum asphaltenes, as well as some model compounds, into catalyst pores at evaluated temperatures and pressures. To achieve this objective we are performing asphaltene diffusion experiments under nonreactive conditions, but at higher temperatures and pressures than normally used in diffusion experiments which are typically conducted near ambient conditions. In our study we are examining the effects of variables such as asphaltene concentrations, solvent type e. g. aliphatic vs. aromatic, and porous media properties, e. g. pore diameter, particle size, on the intrapore diffusion rate. A mathematical model is being used to simulate the results of the diffusion experiments by fitting the model parameters with experimental data.

The above problem is important because asphaltene diffusion into the pores of heterogeneous catalysts is a critical facet involved in the catalytic upgrading of heavy petroleum and coal liquids. In these reactions, the pore diffusional access often limits the overall reaction rates. Because of the comparable sizes of asphaltene molecules and catalyst pores diffusion takes place in the hindered regime, and thus the effectiveness factors in the catalyst pellets can be significantly less than unity. Our project seeks to determine through estimation and mathematical modeling of experimental diffusion data how certain factors such as temperature, concentration, and solvent environment affect the diffusion rate of asphaltene molecules into catalyst pores. The resulting information will be useful in the modeling of chemical reactions involving such species reacting in heterogeneous catalysts, as well as in catalyst and reactor design.

This past year, we have conducted adsorptive uptake experiments for the diffusion of a coal asphaltene into alumina catalyst pellets in the presence of 1-methylnaphthalene solvent at temperatures up to 280° C. These experiments were carried out in a modified high temperature/high pressure autoclave, received from Parr Instrument Company. Earlier, the equipment was verified by performing several runs for the uptake of the model compound quinoline from mineral oil onto Al₂O₃. The effect of external mass transfer was studied

by the uptake of quinoline from mineral oil onto Al_2O_3 at different stirring speeds, and external mass transfer effects were determined to be negligible. A mathematical model with a linear adsorption isotherm and incorporating the diffusion and adsorption mechanisms operating in the uptake system was developed and applied to simulate the experimental adsorptive uptake data. The model incorporates various experimental parameters such as catalyst mass, solvent volume, catalyst properties, and other factors to allow the uptake rates of solute molecules to be correlated. We found that over a fairly wide temperature range of 55 to 280° C, the model fit the experimental data quite well. The diffusivity of asphaltenes in the catalyst pores was estimated from the Stokes-Einstein equation as modified by appropriate factors such as the tortuosity, porosity, and steric hindrance parameters in order to allow for the effects of pore geometry. As a result of fitting the experimental data with the mathematical model, the linear adsorption constant was found to be a logarithmic function of temperature which decreased with increasing temperature. The effects of temperature on the diffusion coefficient and the adsorption were found to be compensating to a certain degree, as might be expected based on observed behavior with temperature in the literature.

In the next time period, we plan to further investigate diffusion and adsorption of model compounds and asphaltenes at higher temperatures and pressures under a variety of experimental conditions. The effects of asphaltene concentration and solvent type, e. g. aliphatic vs. aromatic, will be examined. Appropriate mathematical modeling will be applied to simulate the adsorptive uptake processes in order to model the effects of the adsorption and diffusion parameters on the overall process, especially as a function of temperature.

ARTICLES AND PRESENTATIONS

1. X. Yang and James A. Guin, "Diffusion-controlled Adsorptive Uptake of Coal and Petroleum Asphaltenes into a $\text{NiMo}/\text{Al}_2\text{O}_3$ Hydrotreating Catalyst" *Chemical Engineering Communications*, (1998), in press.
2. X. Yang, "Hindered Diffusion of Model Compounds and Asphaltenes in Fresh and Aged Catalysts Extrudates", PhD Dissertation, Chemical Engineering, Auburn University, 1997.
3. Surya Vadlamani, M. S. Thesis, Auburn University, in progress.

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